Formation of stable iron/cobalt NHC complexes via unexpected ring opening and *in situ* generation of a tridentate ligand†

Gao-Feng Wang,[a] Xiao-Jiao Song,[a] Fei Chen,[a] Yi-Zhi Li,[a] Xue-Tai Chen,[a,]* and Zi-Ling Xue[b,]*

[a] *State Key Laboratory of Coordination Chemistry, Nanjing National Laboratory of Microstructures, School of Chemistry and Chemical Engineering, Nanjing University, Nanjing 210093, China*

[b] *Department of Chemistry, University of Tennessee, Knoxville, Tennessee 37996, USA*

Supplementary materials

*Corresponding authors. Fax: +86-25-83314502. E-mail: xtchen@netra.nju.edu.cn (XTC); xue@utk.edu (ZLX).

General Procedures: The reagents employed were commercially available and used without further purification. Solvents were dried with 4A molecular sieves before use. Elemental analyses were performed on an Elementar Vario ELIII elemental analyzer. NMR spectra were obtained in DMSO-d_6 on a Bruker AM-500 spectrometer. Chemical shifts are given in parts per million for ^{1}H and ^{13}C {H} NMR. The IR spectra were recorded on a Bruker Vector 22 spectrophotometer with KBr pellets in the 4000-400 cm^{-1} region. Cyclic voltammetry measurements were conducted on a model CHI 660 D voltammetric analyzer with a glassy carbon as the working electrode, a polished platinum wire as the counter electrode, $Ag/AgNO_3$ as the reference electrode, and 0.1 M *n*-Bu_4NPF_6 as the supporting electrolyte at a scan rate of 0.1 V/s. Ferrocene was used in each experiment as an internal standard and all potentials are referenced to the ferrocene-ferrocenium couple. The magnetic properties of the products were obtained on superconducting quantum interference device (SQUID) magnetometer (Quantum Design) range of 1.8-300 K and in 2000 Oe. The following starting materials were prepared according to the literature methods: 4,4′-bi-1,2,4-triazole, 1,1′-dimethyl-4,4′-bi-1,2,4-triazolium diiodide and 1,1′-dibutyl-4,4′-bi-1,2,4-triazolium diiodide.[1] **1** (58%), **2** (52%) and **3** (46%) were prepared in a sealed tube when Et_3N was used as a base. Complexes **1-3** can be prepared in air or under an inert atmosphere.

Synthesis of 1,1′-dibutyl-4,4′-bi-1,2,4-triazolium hexafluorophosphate: 1,1′-Dibutyl-4,4′-bi-1,2,4-triazolium diiodide (2.52 g, 5.0 mmol) was dissolved in 200 mL of water. Subsequent addition of NH_4PF_6 (1.96 g, 12 mmol) in 20 mL of water to

the aqueous solution afforded a white precipitate, which was collected by filtration and dried. Yield: 2.57 g, 95%. ^{1}H NMR (500 MHz, DMSO-d_6): 10.69 (s, NC*H*N, 2H), 9.71 (s, NC*H*N, 2H), 4.65 (t, 4H, $^{3}J_{H\text{-}H}$ = 7.0 Hz, C*H*$_2$CH$_2$CH$_2$CH$_3$), 1.91 (m, 4H, CH$_2$C*H*$_2$CH$_2$CH$_3$), 1.41 (m, 4H, CH$_2$CH$_2$C*H*$_2$CH$_3$), 0.98(t, 6H, $^{3}J_{H\text{-}H}$ = 7.0 Hz, CH$_2$CH$_2$CH$_2$C*H*$_3$). ^{13}C NMR (100 MHz, DMSO-d_6): 144.6 (N*C*HN), 144.1 (N*C*HN), 53.1 (N*C*H$_2$), 30.4 (CH$_2$*C*H$_2$CH$_2$CH$_3$), 19.0 (CH$_2$CH$_2$*C*H$_2$CH$_3$), 13.6 (CH$_2$*C*H$_2$CH$_2$*C*H$_3$). Anal. Calcd for $C_{12}H_{22}N_6F_{12}P_2$: C, 26.68; H, 4.10; N, 15.56. Found: C, 26.86; H, 4.15; N, 15.60. IR (KBr, cm^{-1}): *v* 3156, 2965, 1627, 1569, 1465, 1076, 976, 844, 613, 561.

Synthesis of [Fe(L^1)$_2$]I (**1**): A mixture of 1,1′-dimethyl-4,4′-bi-1,2,4-triazolium diiodide (0.42 g, 1.0 mmol), $FeCl_2$ (0.128 g, 1.00 mmol) and K_2CO_3 (0.276 g, 2.0 mmol) in 10 mL of CH_3CN was stirred at 70 °C for 12 h. After cooling to room temperature, the suspension was filtered. The remaining filtrate was allowed to stay in air for two weeks. X-ray quality crystals of **1** were grown from an acetonitrile solution by slow evaporation. Yield: 0.157 g, 56 % (based on the triazolium salt). Anal. Calcd for $C_{12}H_{18}FeIN_{12}O_2$: C, 26.44; H, 3.33; N, 30.83. Found: C, 26.40; H, 3.45; N, 30.75. IR (KBr, cm^{-1}): *v* 1648, 1562, 1396, 1346, 1276, 964, 794. ESI-MS (m/z): $[M-I]^+$, 418.17 (100%).

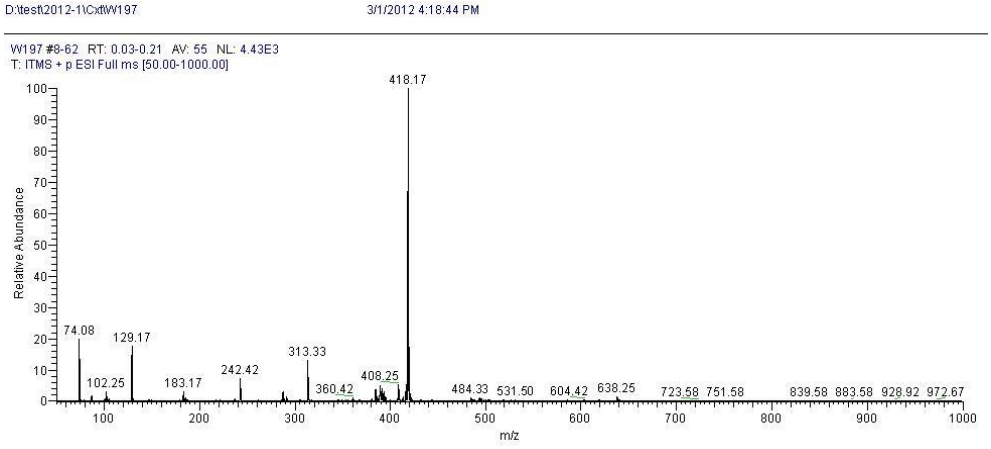
Synthesis of [Fe(L^2)$_2$]PF$_6$ (**2**): The compound was obtained as a dark blue solid using the same procedure as for **1** by using 1, 1′-dibutyl-4, 4′-bi-1, 2, 4-triazolium hexafluorophosphate (0.54 g, 1.0 mmol), $FeCl_2$ (0.128 g, 1.00 mmol) and K_2CO_3 (0.276 g, 2.0 mmol). Crystals suitable for X-ray diffraction study were grown at room

temperature by slow diffusion of diethyl ether into an acetonitrile solution of **2**. Yield: 0.243 g, 63 % (based on the triazolium salt). Anal. Calcd for $C_{24}H_{42}F_6FeN_{12}O_2P$: C, 39.41; H, 5.79; N, 22.98. Found: C, 39.44; H, 5.77; N, 23.09. IR (KBr, cm^{-1}): *v* 3143, 2964, 2874, 1581, 1463, 1427, 1344, 1266, 1169, 1116, 1055, 958, 843, 558, 526, 478. ESI-MS (m/z): $[M-PF_6]^+$, 586.42 (100%).

Synthesis of $[Co(L^1)_2]I$ (3): The compound was obtained as a red crystalline solid using the same procedure as for **1** by using 1,1′-dimethyl-4,4′-bi-1,2,4-triazolium diiodide (0.42 g, 1.0 mmol), $CoCl_2$ (0.14 g, 1.00 mmol) and K_2CO_3 (0.276 g, 2.0 mmol) as the starting material. X-ray quality crystals of **3** were grown from an acetonitrile solution by slow evaporation. Yield: 0.150 g, 53% (based on the triazolium salt). ^{1}H NMR (500 MHz, DMSO-d_6): 9.26 (s, NC*H*O, 1H), 7.99 (s, NC*H*N, 1H), 7.73 (s, NC*H*N, 1H), 3.63 (s, 3H, NCH_3), 3.31 (s, 3H, NCH_3). ^{13}C NMR (125.7MHz, DMSO-d_6): 161.3 (N*C*HN), 150.4 (N*C*N), 145.4 (O*C*HN), 142.4 (N*C*HN), 40.17 (N*C*H_3), 34.9 (N*C*H_3). Anal. Calcd for $C_{12}H_{18}CoIN_{12}O_2$: C, 26.29; H, 3.31; N, 30.66. Found: C, 26.22; H, 3.45; N, 30.56. IR (KBr, cm^{-1}): *v* 3118, 2929, 1631, 1575, 1475, 1347, 1191, 1087, 1049, 944, 844, 792, 733, 609, 522, 484, 435. ESI-MS (m/z): $[M-I]^+$, 421.17 (100%).

Synthesis of $[Fe(L^1)_2]$ (4): To a solution of **1** (0.163 g, 0.30 mmol) in CH_3CN-MeOH (10:1, 11 ml) under an inert atmosphere (N_2), KBH_4 (0.108 g, 2.0 mmol) was added. The reaction mixture was stirred at room temperature for 0.5 h, during which time the color changed from blue to bright red. The solvent is removed in vaccum and the residue is extracted into 20 mL of dry CH_2Cl_2. The resulting mixture is filtered, and

the filtrate is concentrated in vaccum. On addition of 40 mL of dry Et_2O the crude products precipitate. Further purification can be achieved by recrystallization from dry CH_2Cl_2-Et_2O. The product was obtained as air and moisture-sensitive red blocks. Yield: 0.069 g, 55% (based on **1**). ^{1}H NMR (500 MHz, $CDCl_3$): 8.33 (s, NC*H*O, 1H), 7.69 (s, NC*H*N, 1H), 7.56 (s, NC*H*N, 1H), 3.47 (s, 3H, NCH_3), 3.19 (s, 3H, NCH_3). ^{13}C NMR (125.7MHz, $CDCl_3$): 158.1 (N*C*HN), 153.2 (N*C*N), 141.5 (O*C*HN), 140.6 (N*C*HN), 38.4 (NCH_3), 33.4 (NCH_3).Anal. Calcd for $C_{12}H_{18}FeN_{12}O_2$: C, 34.46; H, 4.34; N, 40.19. Found: C, 34.40; H, 4.30; N, 40.13. IR (KBr, cm^{-1}): *v* 1631, 1575, 1465, 1346, 1087, 956, 863, 782, 732, 632, 509.



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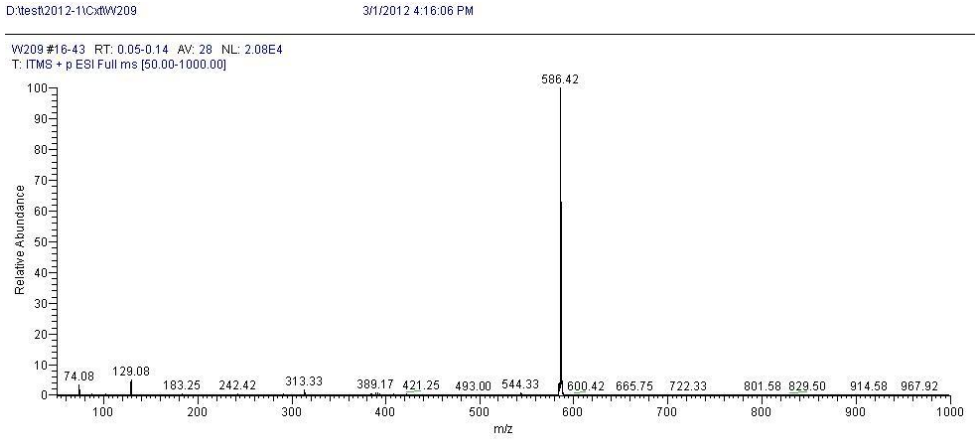

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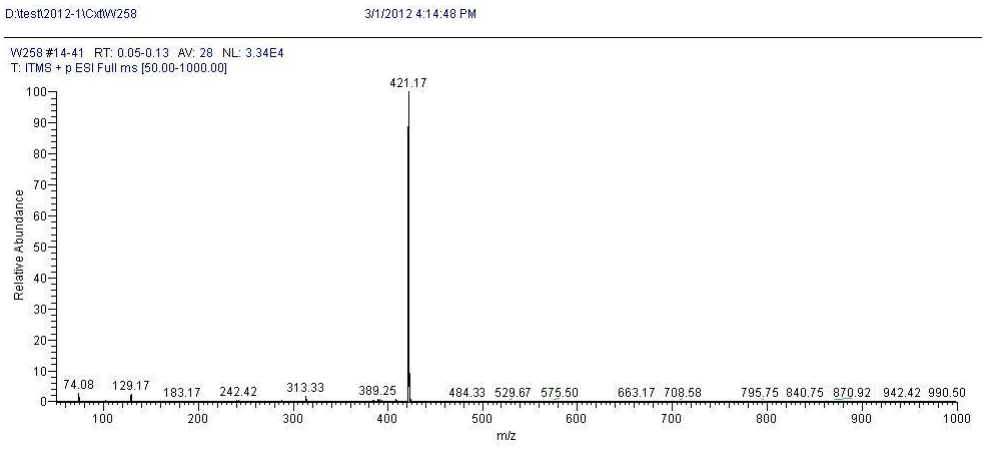


(c)

Fig 1S ESI-MS spectra for (a) **1**, (b) **2** and (c) **3**.

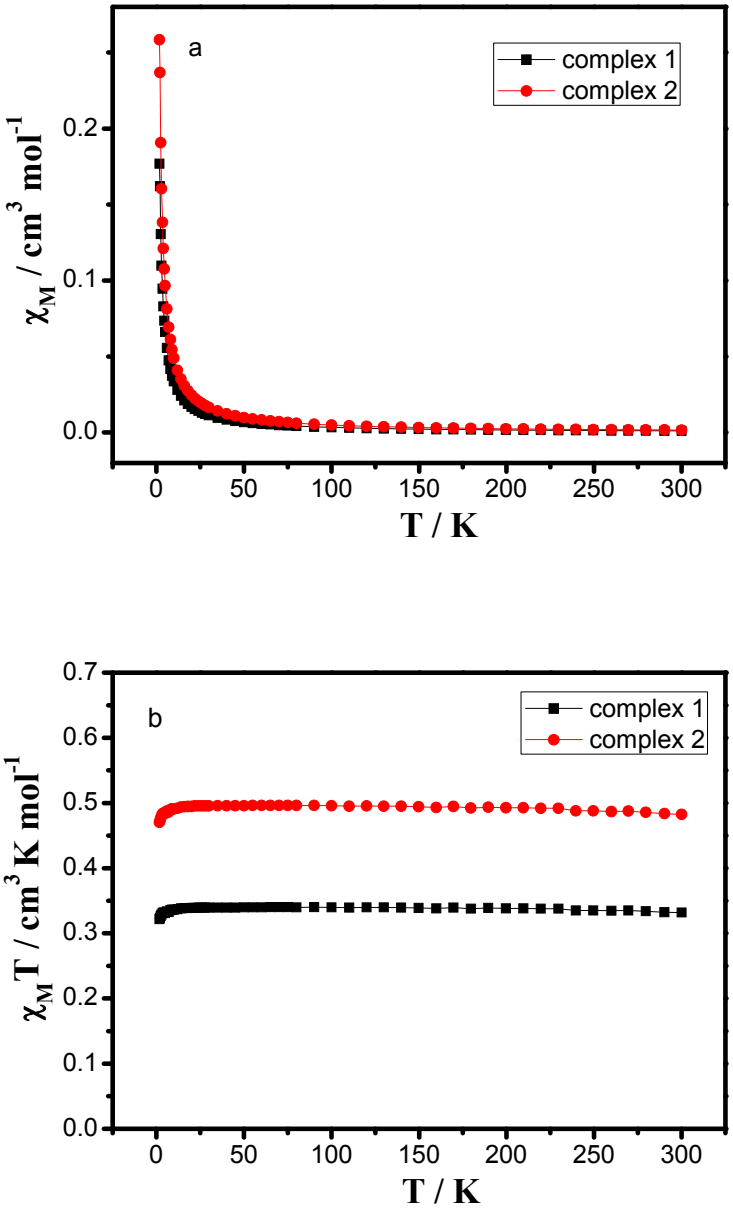
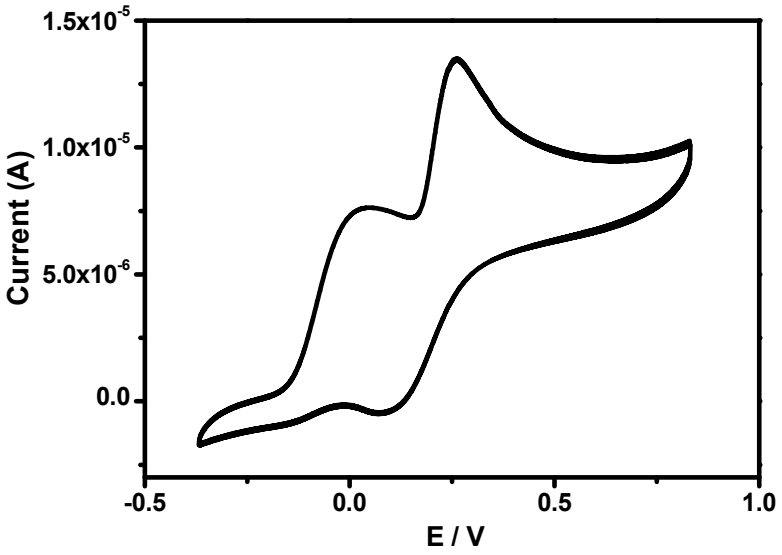
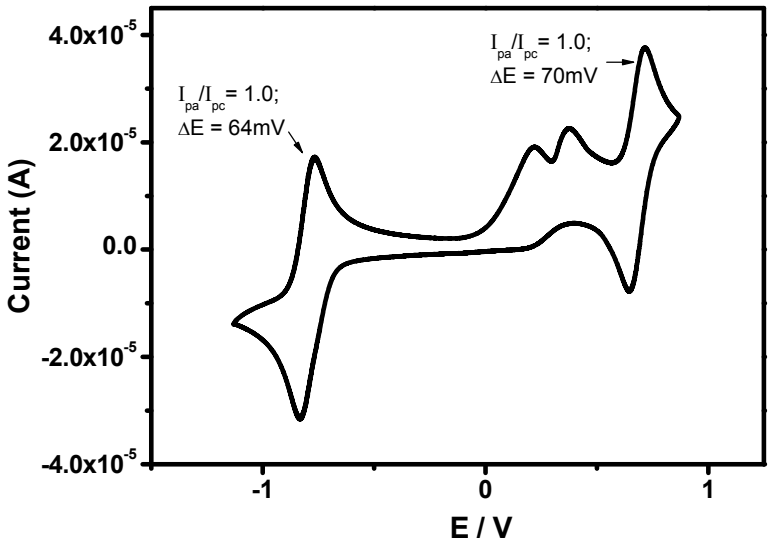


Fig 2S. Temperature dependence of the molar paramagnetic susceptibility, χ_M and $\chi_M T$, for microcrystalline samples of **1** and **2**.



(a)



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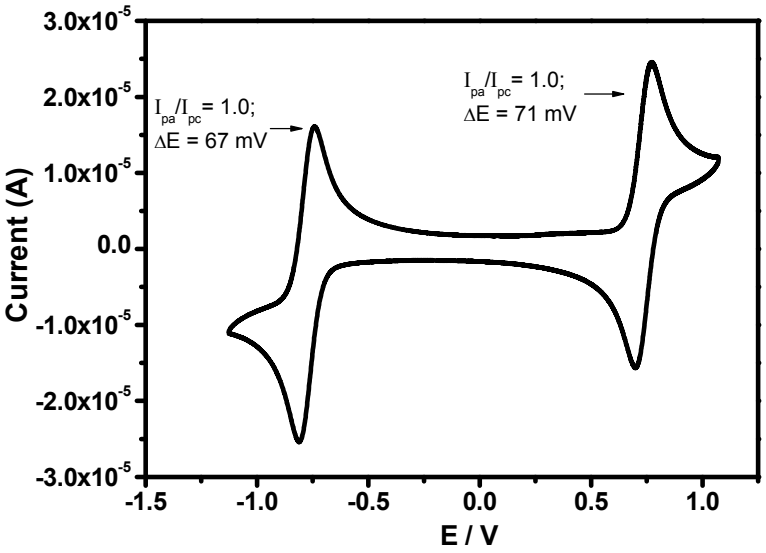

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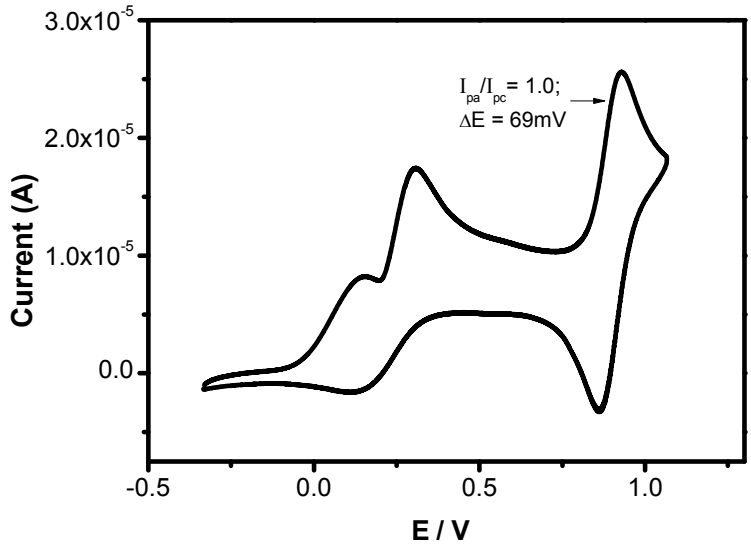

(d)

Fig 3S Cyclic voltammetry curves for a 0.001 M (a) $Bu_4N^+I^-$, (b) **1**, (c) **2**, and (d) **3**, in 0.1 M $Bu_4N^+PF_6^-$ acetonitrile solution, recorded at scan rates = 0.1V s^{-1}, T = 25 ºC, glassy carbon working electrode.

Table 1S. Summary of crystal data and refinement for complexes **1**, **2**, **3** and **4**

Compound	**1**	**2**	**3**	**4**
Formula	$C_{12}H_{20}FeIN_{12}O_3$	$C_{26}H_{45}F_6FeN_{13}O_2P$	$C_{26}H_{39}Co_2I_2N_{25}O_4$	$C_{13}H_{20}FeN_{12}O_2Cl_2$
CCDC no	869061	869062	869060	889218
Formula weight	563.15	772.57	464.69	503.16
T(K)	291(2)	291(2)	291(2)	123(2)
Crystal system	Monoclinic	Triclinic	Monoclinic	Triclinic
Space group	*P*2(1)/n	*P*-1	*C*2/c	*P*-1
a (Å)	7.555(3)	11.6055(17)	19.9487(18)	8.6334(12)
b (Å)	25.707(11)	12.6303(13)	12.1594(13)	8.7729(13)
c (Å)	11.485(5)	12.6377(19)	20.182(2)	14.2422(14)
a (º)	90	98.8230(10)	90	78.270(2)
β (º)	93.827(6)	95.409(2)	107.802(3)	74.950(3)
γ (º)	90	97.5500(10)	90	75.447(2)
V ($Å^{-3}$)	2225.7(16)	1802.2(4)	4661.0(9)	997.2(2)
Z	4	2	4	2
$D_{calc.}$ ($g\ m^{-3}$)	1.681	1.424	1.621	1.676
μ (mm^{-1})	2.103	0.539	2.096	1.065
F (000)	1116	806	2248	516
θ Range (°)	1.95 to 25.68	1.64 to 26.00	1.99 to 25.35	1.50 to 25.35
Restraints/parameters	0 / 284	0 / 447	0 / 284	0 / 275
Reflections collected	11327	9679	12844	6756

Reflections unique	4215	6924	4260	3580
R_{int}	0.0483	0.0258	0.0355	0.0355
Goodness-of-fit on F^2	1.040	1.080	1.034	1.054
R_1/wR_2 [$I > 2\sigma(I)$]	0.0542 / 0.1384	0.0546 / 0.1030	0.0511 / 0.0945	0.0562 / 0.1171
R_1/wR_2 (all data)	0.0791 / 0.1498	0.0909 / 0.1094	0.0632 / 0.0986	0.0732 / 0.1214
Largest peak and hole (e/Å^3)	1.022 / -0.824	0.611 / -0.393	0.820 / -0.697	0.301 / -0.396

Table 2S. Bond lengths (Å) and angles (º) for complex **1**

C(1)-N(1)	1.324(9)
C(1)-N(3)	1.355(8)
C(1)-Fe(1)	1.910(7)
C(2)-N(2)	1.293(9)
C(2)-N(3)	1.360(9)
C(3)-N(4)	1.237(9)
C(3)-N(5)	1.354(8)
C(4)-O(1)	1.267(9)
C(4)-N(6)	1.345(9)
C(5)-N(1)	1.493(9)
C(6)-N(6)	1.462(9)
C(7)-N(7)	1.296(9)
C(7)-N(9)	1.384(9)
C(7)-Fe(1)	1.900(7)
C(8)-N(8)	1.323(9)
C(8)-N(9)	1.354(9)
C(9)-N(10)	1.305(9)
C(9)-N(11)	1.319(9)
C(10)-O(2)	1.271(9)
C(10)-N(12)	1.289(9)
C(11)-N(7)	1.467(11)
C(12)-N(12)	1.428(9)
Fe(1)-N(5)	1.877(6)
Fe(1)-N(11)	1.899(6)
Fe(1)-O(1)	2.027(5)
Fe(1)-O(2)	2.034(5)
N(1)-N(2)	1.350(8)
N(3)-N(4)	1.418(8)

N(5)-N(6)	1.392(8)
N(7)-N(8)	1.418(9)
N(9)-N(10)	1.362(8)
N(11)-N(12)	1.428(8)
N(1)-C(1)-N(3)	101.9(6)
N(1)-C(1)-Fe(1)	134.4(5)
N(3)-C(1)-Fe(1)	123.7(5)
N(2)-C(2)-N(3)	107.4(6)
N(4)-C(3)-N(5)	131.4(8)
O(1)-C(4)-N(6)	121.4(6)
N(7)-C(7)-N(9)	103.8(6)
N(7)-C(7)-Fe(1)	135.0(6)
N(9)-C(7)-Fe(1)	121.2(5)
N(8)-C(8)-N(9)	112.6(6)
N(10)-C(9)-N(11)	126.4(7)
O(2)-C(10)-N(12)	122.5(7)
N(5)-Fe(1)-N(11)	169.5(3)
N(5)-Fe(1)-C(7)	99.4(3)
N(11)-Fe(1)-C(7)	87.7(3)
N(5)-Fe(1)-C(1)	87.8(3)
N(11)-Fe(1)-C(1)	99.3(3)
C(7)-Fe(1)-C(1)	94.9(3)
N(5)-Fe(1)-O(1)	81.6(2)
N(11)-Fe(1)-O(1)	91.2(2)
C(7)-Fe(1)-O(1)	86.9(3)
C(1)-Fe(1)-O(1)	169.4(2)
N(5)-Fe(1)-O(2)	91.6(2)
N(11)-Fe(1)-O(2)	81.2(2)
C(7)-Fe(1)-O(2)	168.9(3)
C(1)-Fe(1)-O(2)	87.0(2)
O(1)-Fe(1)-O(2)	93.16(19)
C(1)-N(1)-N(2)	113.1(6)
C(1)-N(1)-C(5)	129.0(6)
N(2)-N(1)-C(5)	117.7(6)
C(2)-N(2)-N(1)	106.3(6)
C(1)-N(3)-C(2)	110.9(6)
C(1)-N(3)-N(4)	129.6(6)
C(2)-N(3)-N(4)	119.6(5)
C(3)-N(4)-N(3)	114.6(6)
C(3)-N(5)-N(6)	118.1(6)
C(3)-N(5)-Fe(1)	126.6(5)
N(6)-N(5)-Fe(1)	113.6(4)
C(4)-N(6)-N(5)	112.6(6)

C(4)-N(6)-C(6)	123.5(6)
N(5)-N(6)-C(6)	123.3(5)
C(7)-N(7)-N(8)	115.0(7)
C(7)-N(7)-C(11)	128.8(7)
N(8)-N(7)-C(11)	116.2(6)
C(8)-N(8)-N(7)	100.6(6)
C(8)-N(9)-N(10)	120.1(6)
C(8)-N(9)-C(7)	107.9(5)
N(10)-N(9)-C(7)	131.9(6)
C(9)-N(10)-N(9)	116.5(6)
C(9)-N(11)-N(12)	117.2(5)
C(9)-N(11)-Fe(1)	128.4(5)
N(12)-N(11)-Fe(1)	111.7(4)
C(10)-N(12)-C(12)	123.7(7)
C(10)-N(12)-N(11)	113.8(6)
C(12)-N(12)-N(11)	122.4(5)
C(4)-O(1)-Fe(1)	109.4(4)
C(10)-O(2)-Fe(1)	108.6(4)

Table 3S. Bond lengths (Å) and angles (º) for complex **2**

C(1)-C(2)	1.511(5)
C(2)-C(3)	1.534(4)
C(3)-C(4)	1.491(4)
C(4)-N(1)	1.482(4)
C(5)-N(3)	1.366(4)
C(5)-N(1)	1.384(4)
C(5)-Fe(1)	1.916(3)
C(6)-N(2)	1.292(4)
C(6)-N(3)	1.373(4)
C(7)-N(4)	1.291(4)
C(7)-N(5)	1.360(4)
C(8)-O(1)	1.302(4)
C(8)-N(6)	1.318(4)
C(9)-N(6)	1.488(4)
C(9)-C(10)	1.538(5)
C(10)-C(11)	1.521(5)
C(11)-C(12)	1.515(5)
C(13)-C(14)	1.538(4)
C(14)-C(15)	1.540(4)
C(15)-C(16)	1.516(5)
C(16)-N(7)	1.457(4)
C(17)-N(7)	1.376(4)

C(17)-N(9)	1.404(4)
C(17)-Fe(1)	1.888(3)
C(18)-N(8)	1.302(4)
C(18)-N(9)	1.395(4)
C(19)-N(11)	1.320(4)
C(19)-N(10)	1.379(4)
C(20)-O(2)	1.240(4)
C(20)-N(12)	1.337(4)
C(21)-N(12)	1.494(4)
C(21)-C(22)	1.506(5)
C(22)-C(23)	1.516(5)
C(23)-C(24)	1.551(5)
C(25)-C(26)	1.470(5)
C(26)-N(13)	1.168(4)
F(1)-P(1)	1.5409(19)
F(2)-P(1)	1.565(2)
F(3)-P(1)	1.6096(19)
F(4)-P(1)	1.526(2)
F(5)-P(1)	1.5953(19)
F(6)-P(1)	1.5238(19)
Fe(1)-N(11)	1.901(3)
Fe(1)-N(5)	1.910(3)
Fe(1)-O(1)	2.013(2)
Fe(1)-O(2)	2.038(2)
N(1)-N(2)	1.391(4)
N(3)-N(4)	1.420(4)
N(5)-N(6)	1.404(4)
N(7)-N(8)	1.397(4)
N(9)-N(10)	1.397(3)
N(11)-N(12)	1.425(3)

C(1)-C(2)-C(3)	116.9(3)
C(4)-C(3)-C(2)	109.2(3)
N(1)-C(4)-C(3)	111.8(3)
N(3)-C(5)-N(1)	101.6(3)
N(3)-C(5)-Fe(1)	124.4(2)
N(1)-C(5)-Fe(1)	134.0(2)
N(2)-C(6)-N(3)	111.8(3)
N(4)-C(7)-N(5)	130.0(3)
O(1)-C(8)-N(6)	122.7(3)
N(6)-C(9)-C(10)	111.4(2)
C(11)-C(10)-C(9)	113.3(3)
C(12)-C(11)-C(10)	121.9(3)
C(13)-C(14)-C(15)	113.7(3)

C(16)-C(15)-C(14)	114.5(3)
N(7)-C(16)-C(15)	113.4(3)
N(7)-C(17)-N(9)	102.4(3)
N(7)-C(17)-Fe(1)	135.2(3)
N(9)-C(17)-Fe(1)	122.4(2)
N(8)-C(18)-N(9)	111.5(3)
N(11)-C(19)-N(10)	123.9(3)
O(2)-C(20)-N(12)	122.2(3)
N(12)-C(21)-C(22)	122.3(3)
C(21)-C(22)-C(23)	117.2(3)
C(22)-C(23)-C(24)	101.4(3)
N(13)-C(26)-C(25)	179.3(4)
C(17)-Fe(1)-N(11)	88.32(13)
C(17)-Fe(1)-N(5)	99.14(13)
N(11)-Fe(1)-N(5)	167.56(11)
C(17)-Fe(1)-C(5)	93.70(14)
N(11)-Fe(1)-C(5)	100.74(13)
N(5)-Fe(1)-C(5)	88.76(13)
C(17)-Fe(1)-O(1)	90.19(12)
N(11)-Fe(1)-O(1)	88.42(10)
N(5)-Fe(1)-O(1)	81.66(10)
C(5)-Fe(1)-O(1)	170.13(12)
C(17)-Fe(1)-O(2)	168.53(12)
N(11)-Fe(1)-O(2)	80.21(10)
N(5)-Fe(1)-O(2)	92.16(10)
C(5)-Fe(1)-O(2)	88.46(11)
O(1)-Fe(1)-O(2)	89.52(9)
C(5)-N(1)-N(2)	113.2(3)
C(5)-N(1)-C(4)	128.6(3)
N(2)-N(1)-C(4)	118.2(2)
C(6)-N(2)-N(1)	103.6(3)
C(5)-N(3)-C(6)	109.8(3)
C(5)-N(3)-N(4)	130.4(3)
C(6)-N(3)-N(4)	119.7(3)
C(7)-N(4)-N(3)	115.4(3)
C(7)-N(5)-N(6)	118.1(3)
C(7)-N(5)-Fe(1)	127.7(2)
N(6)-N(5)-Fe(1)	113.3(2)
C(8)-N(6)-N(5)	112.5(3)
C(8)-N(6)-C(9)	121.7(3)
N(5)-N(6)-C(9)	125.9(3)
C(17)-N(7)-N(8)	113.2(3)
C(17)-N(7)-C(16)	128.8(3)
N(8)-N(7)-C(16)	117.8(2)

C(18)-N(8)-N(7)	104.6(2)
C(18)-N(9)-N(10)	121.2(2)
C(18)-N(9)-C(17)	108.3(2)
N(10)-N(9)-C(17)	130.4(2)
C(19)-N(10)-N(9)	116.3(2)
C(19)-N(11)-N(12)	113.9(3)
C(19)-N(11)-Fe(1)	129.7(2)
N(12)-N(11)-Fe(1)	113.30(19)
C(20)-N(12)-N(11)	111.7(3)
C(20)-N(12)-C(21)	125.2(3)
N(11)-N(12)-C(21)	122.4(2)
C(8)-O(1)-Fe(1)	108.8(2)
C(20)-O(2)-Fe(1)	110.6(2)
F(6)-P(1)-F(4)	91.91(12)
F(6)-P(1)-F(1)	178.26(13)
F(4)-P(1)-F(1)	89.54(11)
F(6)-P(1)-F(2)	90.56(12)
F(4)-P(1)-F(2)	177.50(12)
F(1)-P(1)-F(2)	87.99(12)
F(6)-P(1)-F(5)	87.59(10)
F(4)-P(1)-F(5)	89.21(11)
F(1)-P(1)-F(5)	93.39(11)
F(2)-P(1)-F(5)	90.54(10)
F(6)-P(1)-F(3)	91.06(11)
F(4)-P(1)-F(3)	92.61(11)
F(1)-P(1)-F(3)	87.91(11)
F(2)-P(1)-F(3)	87.71(11)
F(5)-P(1)-F(3)	177.77(11)

Table 4S. Bond lengths (Å) and angles (º) for complex **3**

C(1)-N(1)	1.326(5)
C(1)-N(3)	1.350(5)
C(1)-Co(1)	1.899(4)
C(2)-N(2)	1.293(5)
C(2)-N(3)	1.358(5)
C(3)-N(4)	1.292(5)
C(3)-N(5)	1.321(5)
C(4)-O(2)	1.255(5)
C(4)-N(6)	1.317(5)
C(5)-N(6)	1.460(4)
C(6)-N(1)	1.463(5)
C(7)-N(7)	1.333(6)

C(7)-N(9)	1.340(5)
C(7)-Co(1)	1.883(4)
C(8)-N(8)	1.295(5)
C(8)-N(9)	1.338(5)
C(9)-N(10)	1.278(5)
C(9)-N(11)	1.325(5)
C(10)-N(12)	1.298(5)
C(10)-O(1)	1.299(5)
C(11)-N(12)	1.430(5)
C(12)-N(7)	1.472(5)
C(13)-C(14)	1.437(13)
C(14)-N(13)	1.214(12)
Co(1)-N(11)	1.878(3)
Co(1)-N(5)	1.894(3)
Co(1)-O(1)	1.966(3)
Co(1)-O(2)	1.993(3)
N(1)-N(2)	1.420(5)
N(3)-N(4)	1.400(4)
N(5)-N(6)	1.399(4)
N(7)-N(8)	1.371(5)
N(9)-N(10)	1.413(5)
N(11)-N(12)	1.443(4)
N(13)-N(13)#1	1.820(17)
N(1)-C(1)-N(3)	104.9(3)
N(1)-C(1)-Co(1)	133.3(3)
N(3)-C(1)-Co(1)	121.8(3)
N(2)-C(2)-N(3)	111.4(3)
N(4)-C(3)-N(5)	128.8(3)
O(2)-C(4)-N(6)	121.2(3)
N(7)-C(7)-N(9)	103.2(3)
N(7)-C(7)-Co(1)	134.2(3)
N(9)-C(7)-Co(1)	122.5(3)
N(8)-C(8)-N(9)	110.6(4)
N(10)-C(9)-N(11)	127.1(4)
N(13)-C(14)-C(13)	179.4(9)
N(11)-Co(1)-C(7)	88.73(15)
N(11)-Co(1)-N(5)	169.12(14)
C(7)-Co(1)-N(5)	97.73(15)
N(11)-Co(1)-C(1)	98.14(16)
C(7)-Co(1)-C(1)	92.86(18)
N(5)-Co(1)-C(1)	90.30(15)
N(11)-Co(1)-O(1)	83.15(12)
C(7)-Co(1)-O(1)	171.83(14)

N(5)-Co(1)-O(1)	90.14(12)
C(1)-Co(1)-O(1)	89.26(14)
N(11)-Co(1)-O(2)	89.08(13)
C(7)-Co(1)-O(2)	89.82(15)
N(5)-Co(1)-O(2)	82.23(11)
C(1)-Co(1)-O(2)	172.34(13)
O(1)-Co(1)-O(2)	89.08(11)
C(1)-N(1)-N(2)	111.2(3)
C(1)-N(1)-C(6)	130.7(3)
N(2)-N(1)-C(6)	117.5(3)
C(2)-N(2)-N(1)	103.4(3)
C(1)-N(3)-C(2)	108.8(3)
C(1)-N(3)-N(4)	132.9(3)
C(2)-N(3)-N(4)	118.1(3)
C(3)-N(4)-N(3)	115.5(3)
C(3)-N(5)-N(6)	118.0(3)
C(3)-N(5)-Co(1)	128.3(3)
N(6)-N(5)-Co(1)	111.5(2)
C(4)-N(6)-N(5)	114.6(3)
C(4)-N(6)-C(5)	122.9(3)
N(5)-N(6)-C(5)	122.6(3)
C(7)-N(7)-N(8)	112.5(3)
C(7)-N(7)-C(12)	129.4(3)
N(8)-N(7)-C(12)	118.1(3)
C(8)-N(8)-N(7)	103.8(3)
C(8)-N(9)-C(7)	109.8(3)
C(8)-N(9)-N(10)	119.9(3)
C(7)-N(9)-N(10)	130.3(3)
C(9)-N(10)-N(9)	116.0(3)
C(9)-N(11)-N(12)	116.9(3)
C(9)-N(11)-Co(1)	127.6(3)
N(12)-N(11)-Co(1)	111.3(2)
C(10)-N(12)-C(11)	124.0(3)
C(10)-N(12)-N(11)	113.7(3)
C(11)-N(12)-N(11)	122.2(3)
C(14)-N(13)-N(13)#1	150.2(6)
C(10)-O(1)-Co(1)	110.5(2)
C(4)-O(2)-Co(1)	110.5(2)

Symmetry transformations used to generate equivalent atoms: #1: -x+1, y, -z+3/2

Table 5S. Bond lengths (Å) and angles (º) for complex **4**

C(1)-N(1)	1.372(5)
C(1)-N(3)	1.390(5)

C(1)-Fe(1)	1.888(4)
C(2)-N(2)	1.333(5)
C(2)-N(3)	1.394(5)
C(3)-N(4)	1.329(5)
C(3)-N(5)	1.346(5)
C(4)-O(1)	1.227(5)
C(4)-N(6)	1.323(5)
C(5)-N(6)	1.458(5)
C(6)-N(1)	1.458(5)
C(7)-N(7)	1.356(6)
C(7)-N(9)	1.379(6)
C(7)-Fe(1)	1.918(5)
C(8)-N(8)	1.304(5)
C(8)-N(9)	1.382(5)
C(9)-N(10)	1.332(5)
C(9)-N(11)	1.366(6)
C(10)-O(2)	1.236(5)
C(10)-N(12)	1.353(6)
C(11)-N(12)	1.436(5)
C(12)-N(7)	1.454(5)
C(13)-Cl(2)	1.661(5)
C(13)-Cl(1)	1.757(4)
Fe(1)-N(11)	1.931(3)
Fe(1)-N(5)	1.934(4)
Fe(1)-O(1)	2.020(3)
Fe(1)-O(2)	2.060(3)
N(1)-N(2)	1.394(5)
N(3)-N(4)	1.398(5)
N(5)-N(6)	1.426(5)
N(7)-N(8)	1.405(5)
N(9)-N(10)	1.406(5)
N(11)-N(12)	1.419(5)

N(1)-C(1)-N(3)	100.5(3)
N(1)-C(1)-Fe(1)	134.6(3)
N(3)-C(1)-Fe(1)	125.0(3)
N(2)-C(2)-N(3)	109.8(3)
N(4)-C(3)-N(5)	128.0(4)
O(1)-C(4)-N(6)	123.8(4)
N(7)-C(7)-N(9)	101.4(4)
N(7)-C(7)-Fe(1)	135.6(3)
N(9)-C(7)-Fe(1)	123.0(3)
N(8)-C(8)-N(9)	112.2(4)
N(10)-C(9)-N(11)	126.0(4)

O(2)-C(10)-N(12)	126.1(4)
Cl(2)-C(13)-Cl(1)	115.9(2)
C(1)-Fe(1)-C(7)	91.41(19)
C(1)-Fe(1)-N(11)	101.72(15)
C(7)-Fe(1)-N(11)	89.97(17)
C(1)-Fe(1)-N(5)	88.47(15)
C(7)-Fe(1)-N(5)	100.36(18)
N(11)-Fe(1)-N(5)	165.36(15)
C(1)-Fe(1)-O(1)	169.44(14)
C(7)-Fe(1)-O(1)	93.07(16)
N(11)-Fe(1)-O(1)	87.85(13)
N(5)-Fe(1)-O(1)	81.31(13)
C(1)-Fe(1)-O(2)	93.62(14)
C(7)-Fe(1)-O(2)	170.29(17)
N(11)-Fe(1)-O(2)	80.89(13)
N(5)-Fe(1)-O(2)	88.07(13)
O(1)-Fe(1)-O(2)	83.40(11)
C(1)-N(1)-N(2)	115.6(3)
C(1)-N(1)-C(6)	126.5(3)
N(2)-N(1)-C(6)	116.9(3)
C(2)-N(2)-N(1)	103.1(3)
C(1)-N(3)-C(2)	110.9(3)
C(1)-N(3)-N(4)	132.7(3)
C(2)-N(3)-N(4)	116.4(3)
C(3)-N(4)-N(3)	114.5(3)
C(3)-N(5)-N(6)	116.7(3)
C(3)-N(5)-Fe(1)	130.6(3)
N(6)-N(5)-Fe(1)	111.3(3)
C(4)-N(6)-N(5)	112.8(3)
C(4)-N(6)-C(5)	126.1(4)
N(5)-N(6)-C(5)	121.1(3)
C(7)-N(7)-N(8)	115.2(3)
C(7)-N(7)-C(12)	127.1(4)
N(8)-N(7)-C(12)	117.3(3)
C(8)-N(8)-N(7)	101.9(3)
C(7)-N(9)-C(8)	109.2(3)
C(7)-N(9)-N(10)	133.1(4)
C(8)-N(9)-N(10)	117.6(3)
C(9)-N(10)-N(9)	116.7(4)
C(9)-N(11)-N(12)	114.3(3)
C(9)-N(11)-Fe(1)	130.4(3)
N(12)-N(11)-Fe(1)	114.1(2)
C(10)-N(12)-N(11)	110.1(3)
C(10)-N(12)-C(11)	125.1(4)

N(11)-N(12)-C(11)	124.8(3)
C(4)-O(1)-Fe(1)	110.6(3)
C(10)-O(2)-Fe(1)	108.6(3)

1. M. Poyatos, W. McNamara, C. Incarvito, E. Peris and R. H. Crabtree, *Chem. Commun.*, 2007, 2267-2269.